

The structure of liquid films, droplets and interfaces

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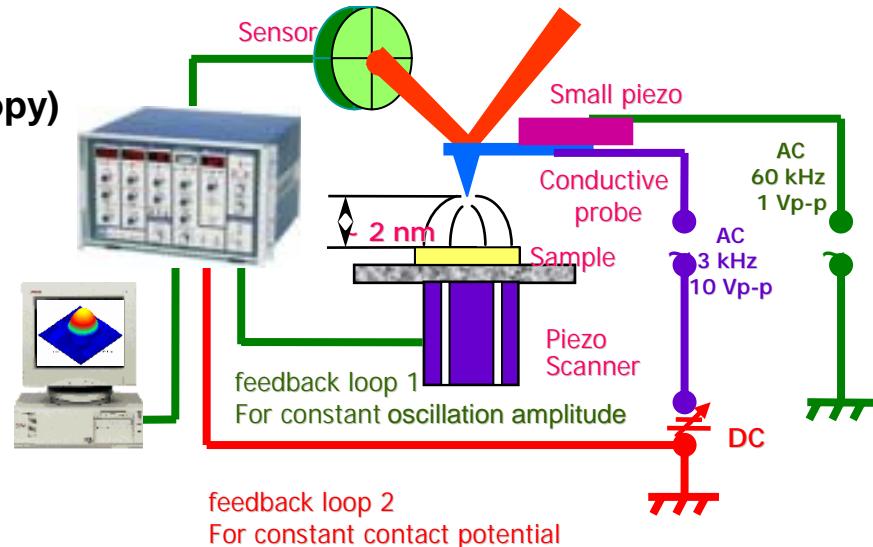
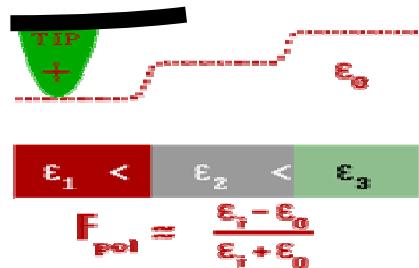
WORKSHOP ON MESOSCOPIC AND NANOSCOPIC SCIENCE
USING X-RAY TECHNIQUES
The Abbey, Lake Geneva, Wisconsin
August 29 - September 1, 2004



AFM techniques to study liquids

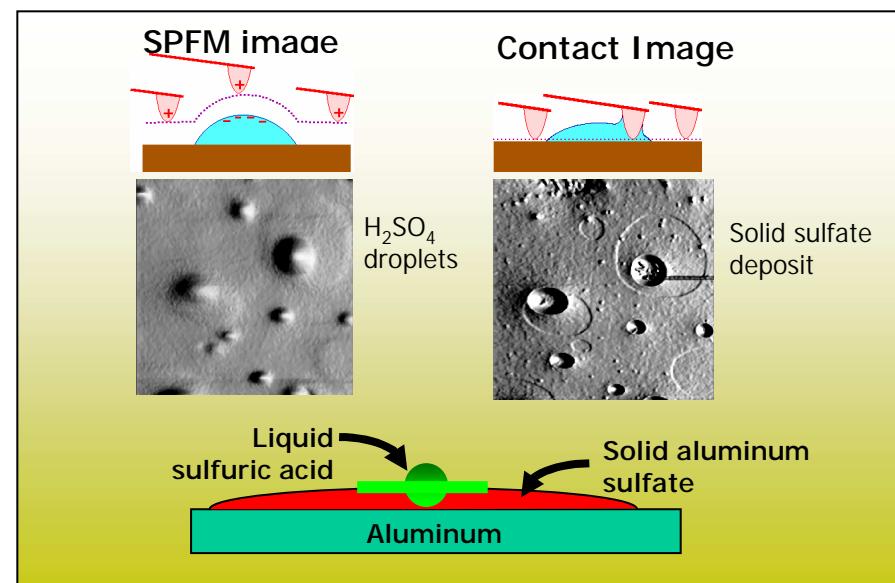
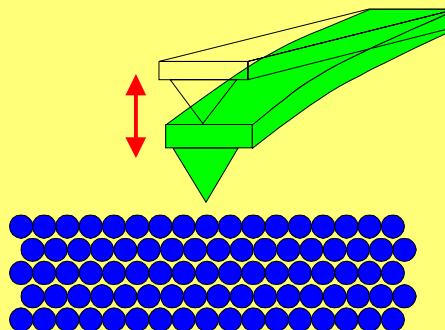
Use of electrostatic Forces (Scanning Polarization Force Microscopy)

Contrast

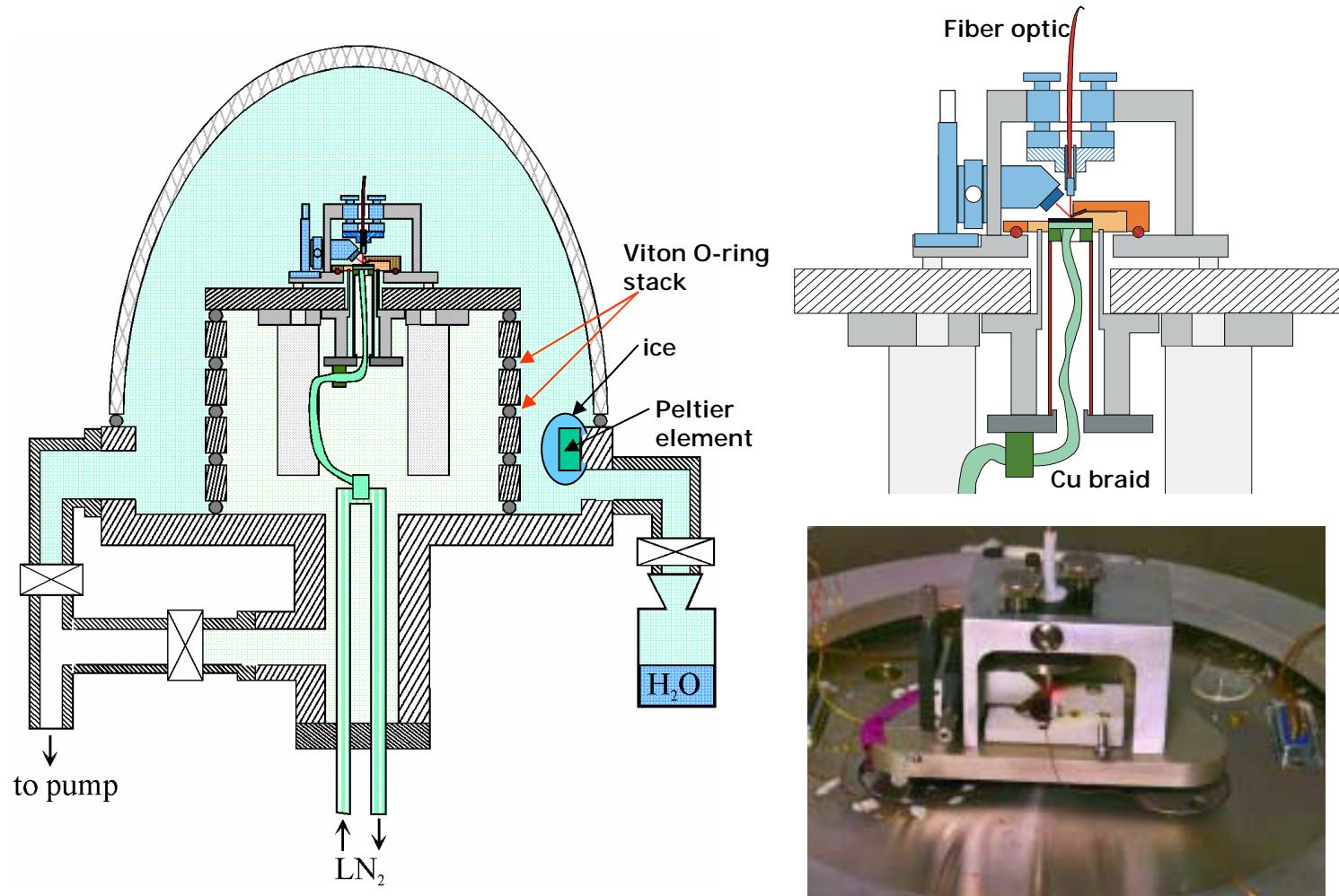


Dielectric Spectroscopy *Freq. Dependence of ε(ω)*

Mechanical modulation

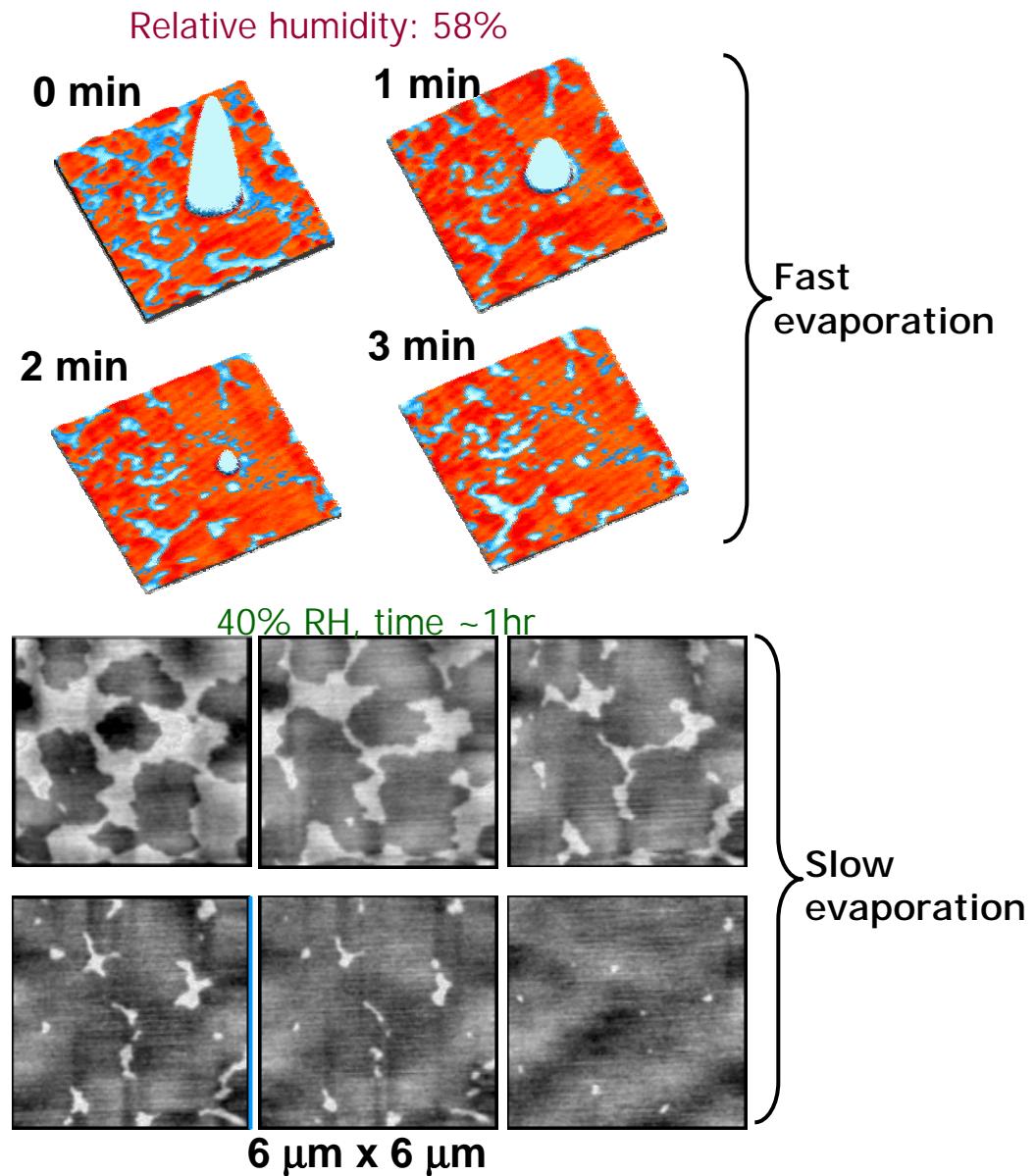
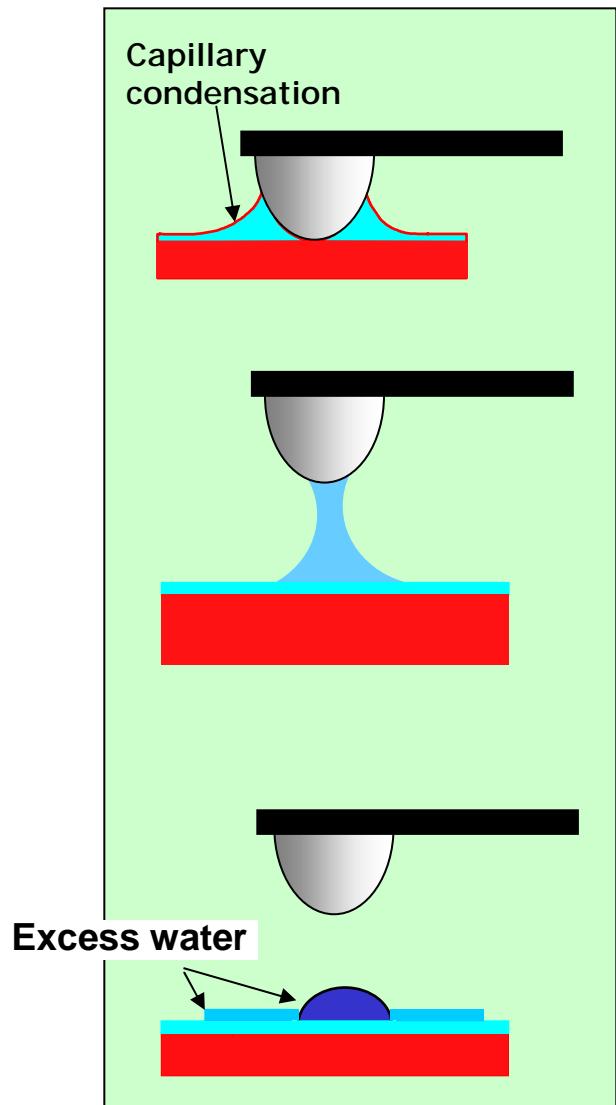


AFM microscope and chamber for liquid /vapor interface studies

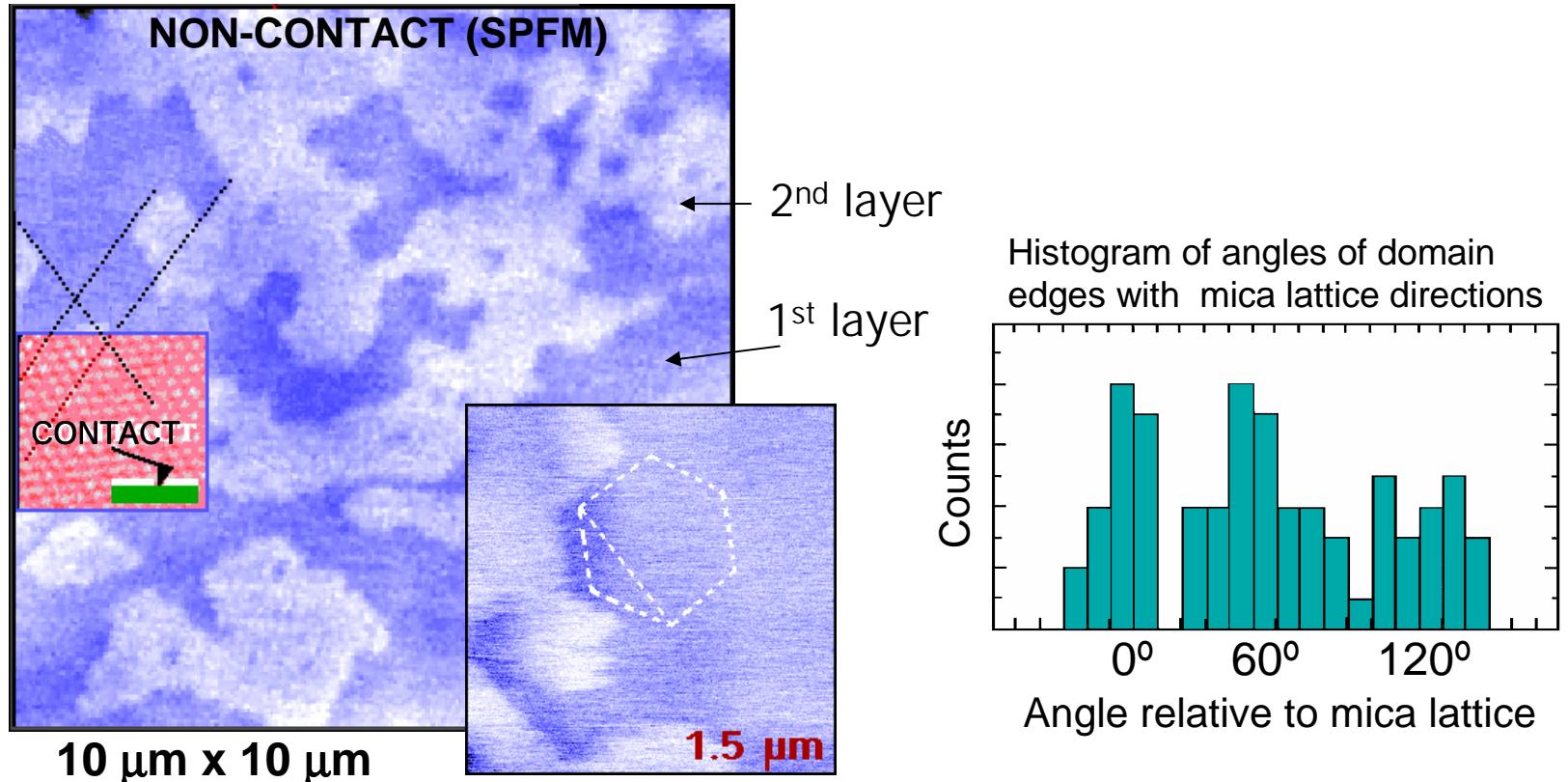


Scanning force microscope and vacuum chamber for the study of ice films: Design and first results
H. Bluhm, S.H. Pan, L. Xu, T. Inoue, D.F. Ogletree and M. Salmeron. *Rev. Sci. Instrum.* 69, 1781 (1998).

Deposition and evaporation of water on mica

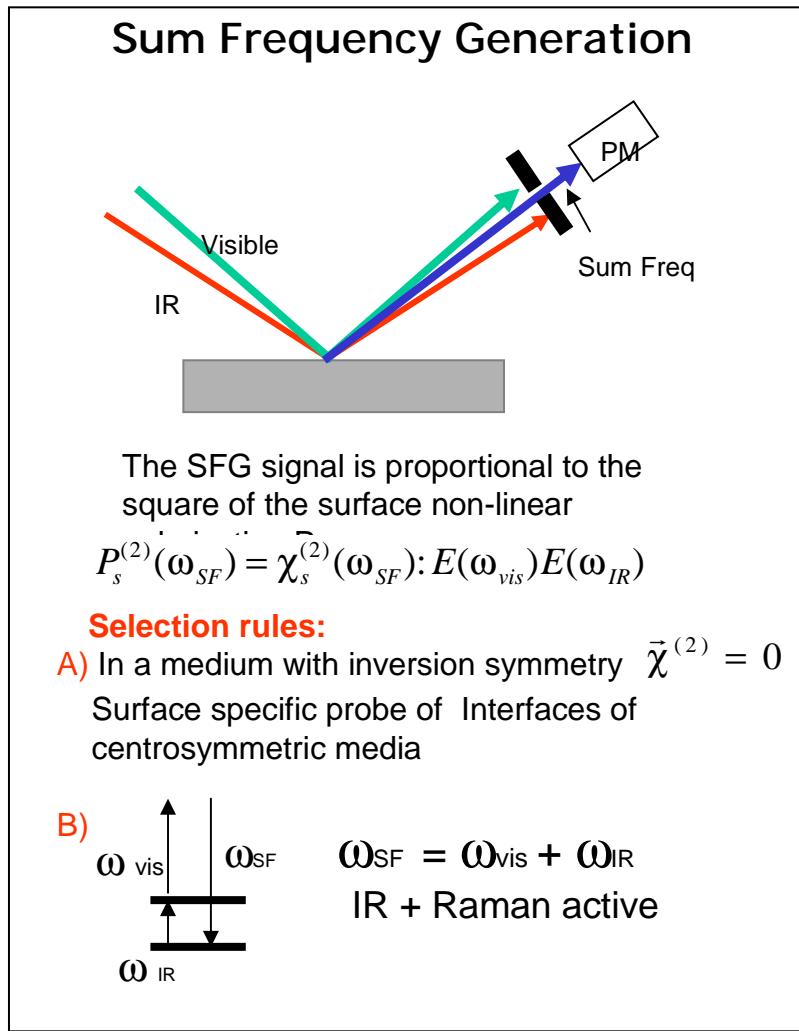


Epitaxial relationship between the water layer and the mica substrate

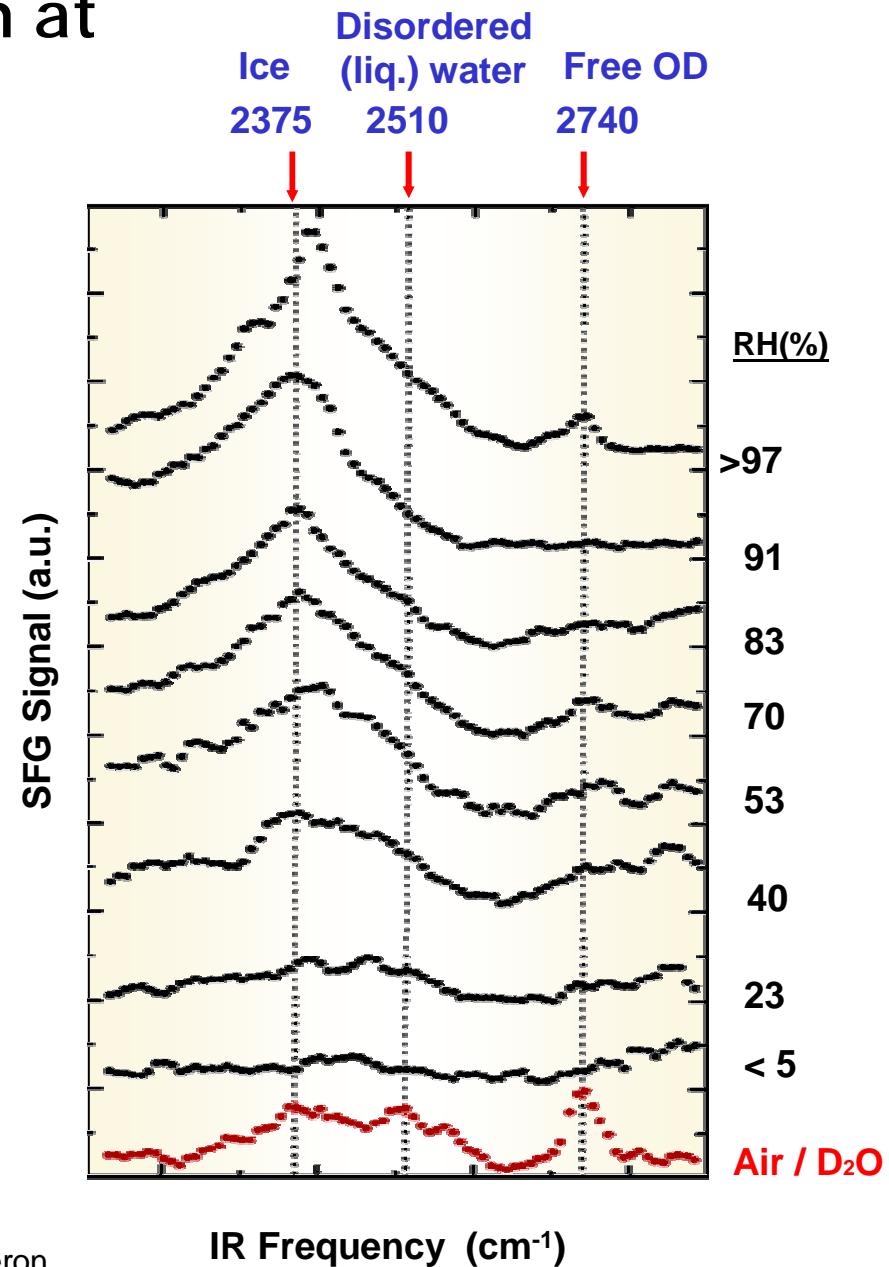


Imaging the condensation and evaporation of molecularly thin films of water with nanometer resolution. J. Hu, X.-d. Xiao, D.F. Ogletree and M. Salmeron. *Science* 268, 267 (1995).

Sum Frequency Generation at the mica/vapor interface



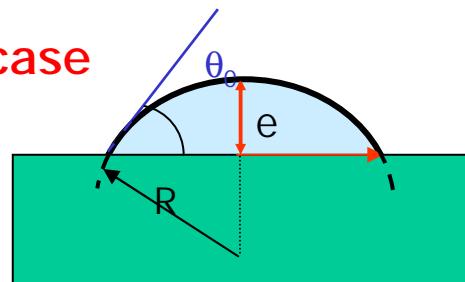
Ice-like water monolayer adsorbed on mica at room temperature. P.B. Miranda, L. Xu, Y.R. Shen and M. Salmeron. Phys. Rev. Lett. 81, 5876 (1998)



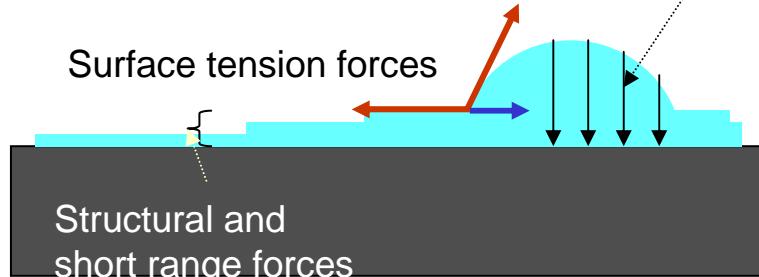
Surface Forces determine the structure of liquid films at the submicrometer scale

Macroscopic case

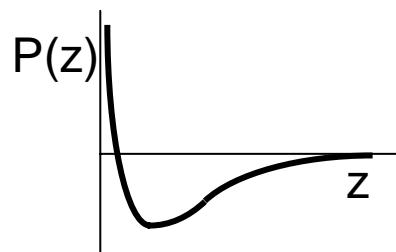
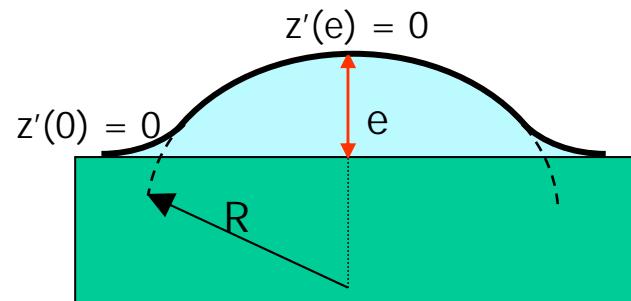
$$\theta_0^2 = 2e/R$$



Van der Waals & double layer forces



Microscopic case

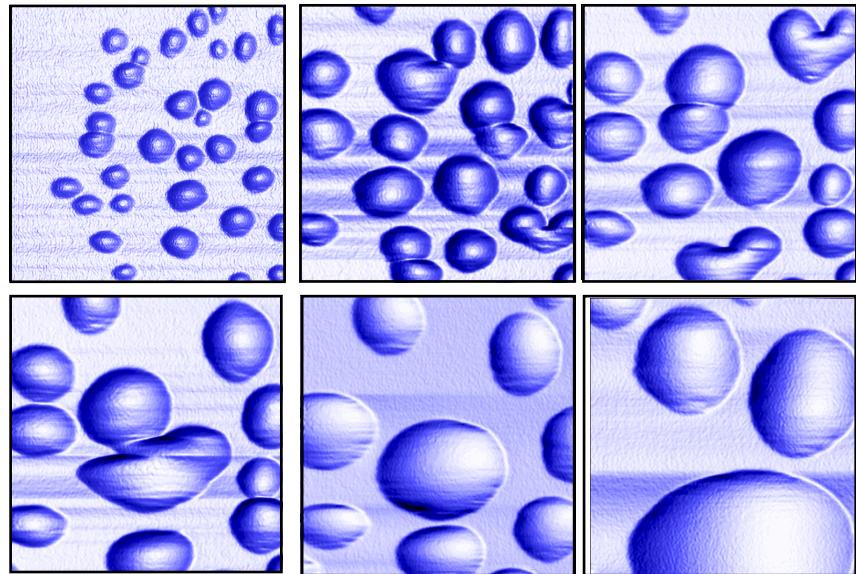


Disjoining pressure $\Pi_e = - \partial P_e / \partial z$

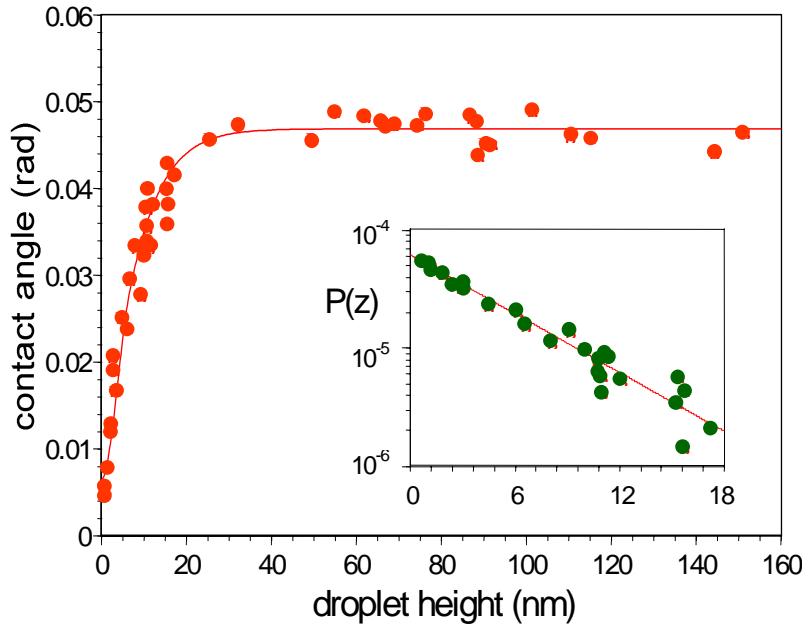
Defining: $\theta^2 = 2e/R \rightarrow \theta^2 = \theta_0^2 + 2(P_e + e \cdot \Pi_e)/\gamma$

Growth of glycerol films on mica from supersaturated vapor

$$\theta^2 = \theta_0^2 + 2(P_e + e \cdot \Pi_e) / \gamma$$



15 μm x 15 μm

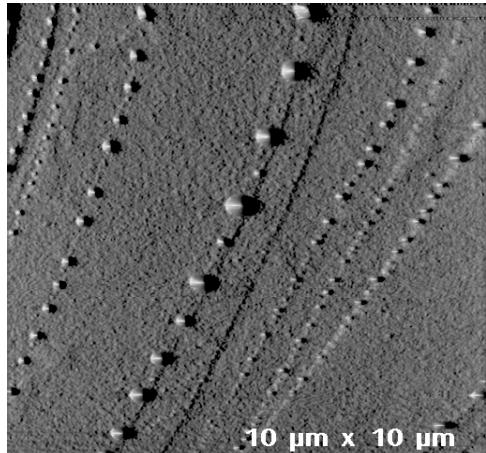


Inset: fit to $P(z) = P_0 \cdot e^{-\frac{z}{a}}$

$$P_0 = -6.5 \times 10^{-5} \text{ J/m}^2 \quad a = 5 \text{ nm}$$

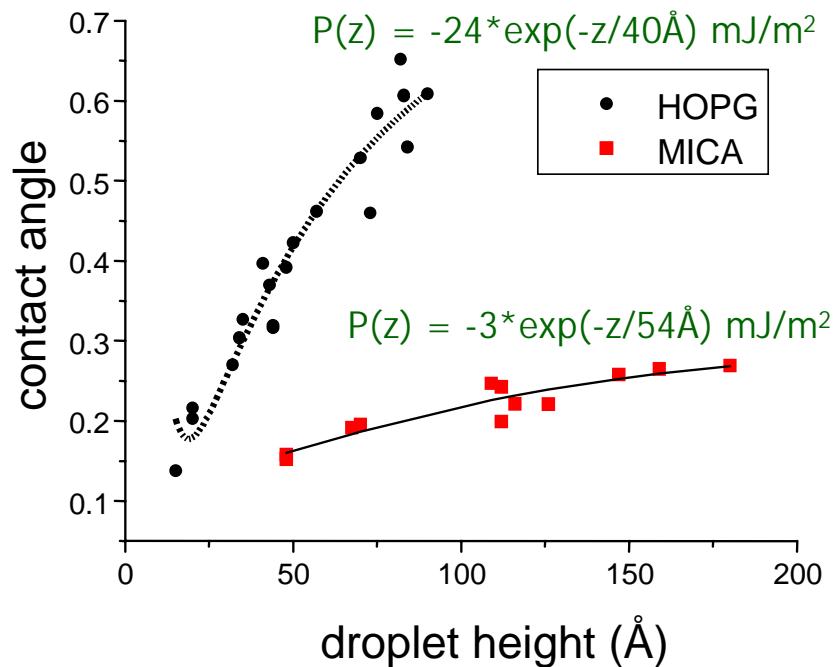
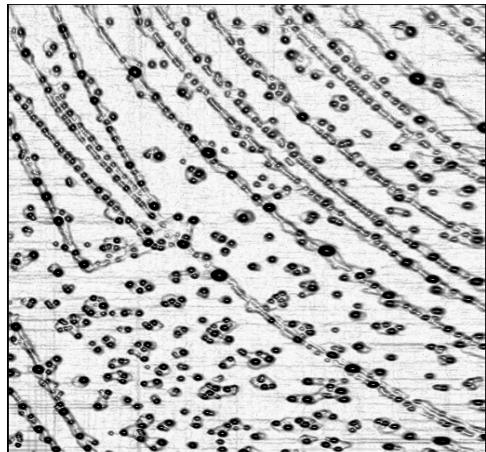
Scanning polarization force microscopy study of the condensation and wetting properties of glycerol on mica. L. Xu and M. Salmeron. *J. Phys. Chem. B* 102, 7210 (1998).

Hydrophobic surfaces



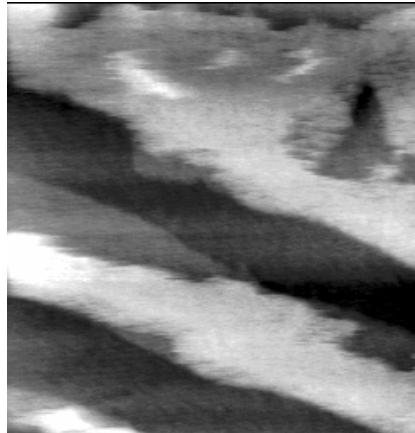
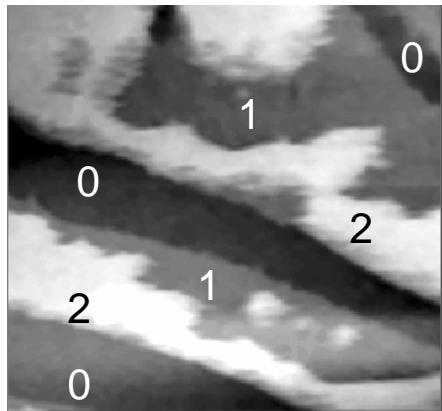
**Water KOH solutions
on graphite**

Liquid droplets preferentially
attach to steps

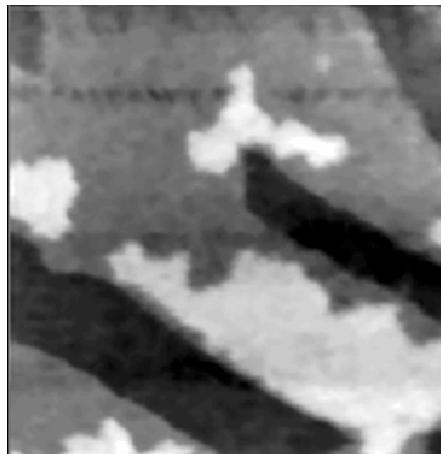


Layering, mobility, de-wetting of Zdol-TX layers on hard discs

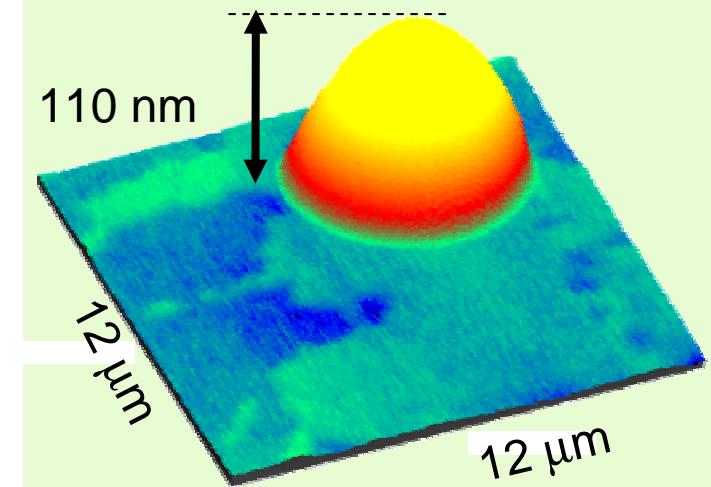
Electrostatic force moves 2nd layer but not 1st



Contact moves both layers

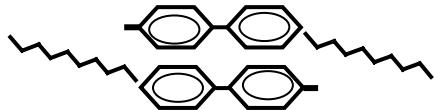


De-wetting: drop growth at the expense of 2nd layer

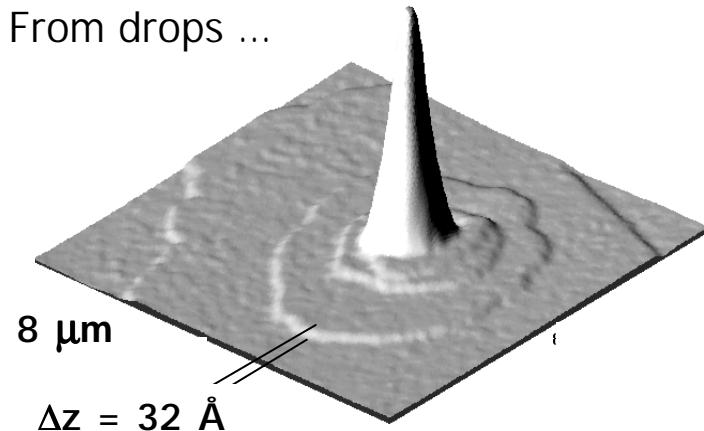


Spreading of 8CB liquid crystal on Si

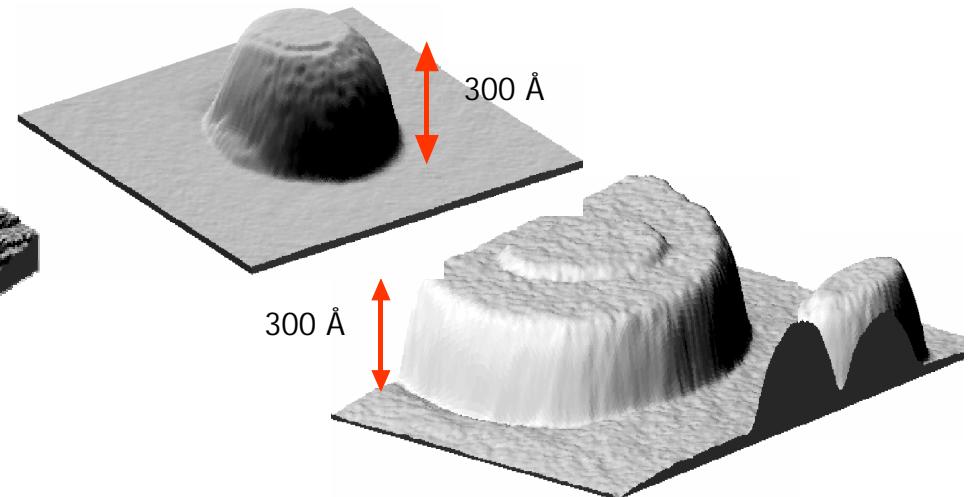
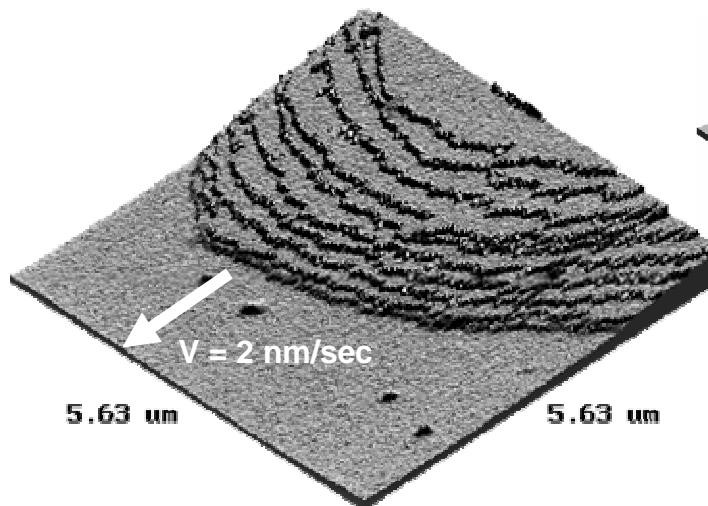
Pairing of 8CB molecules into dimers



From drops ...



.. to final stage of smectic pancakes

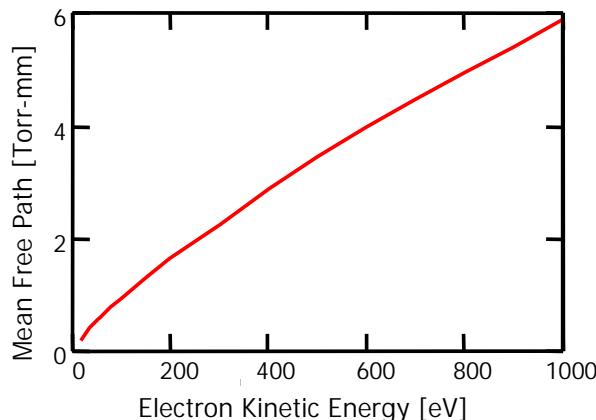


Ambient pressure Photoelectron Spectroscopy

Ambient pressure Photoelectron Spectroscopy

Problem: Scattering of electrons by gas phase molecules

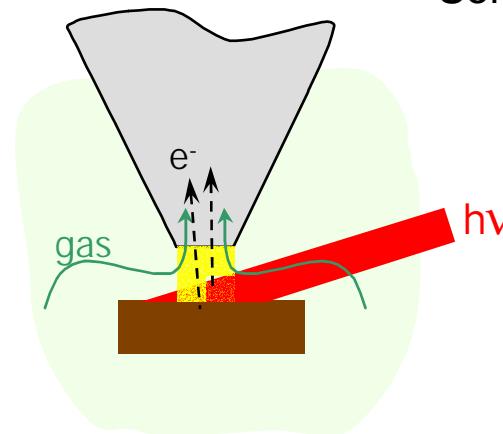
Elastic Mean Free Path in Oxygen Gas



For 500 eV electrons
P ~ 4 Torr for a 1 mm travel
P ~ 45 Torr for a 0.1 mm travel

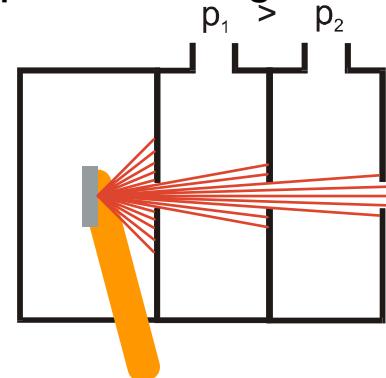


Mark-I @ ALS 9.3.2



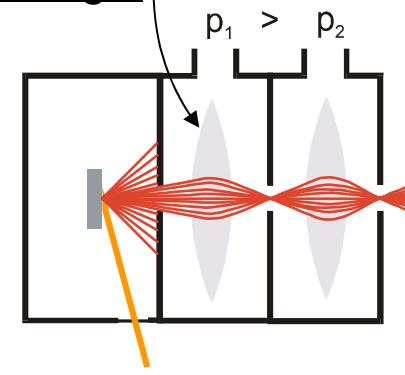
Solution: differential pumping:

previous designs:

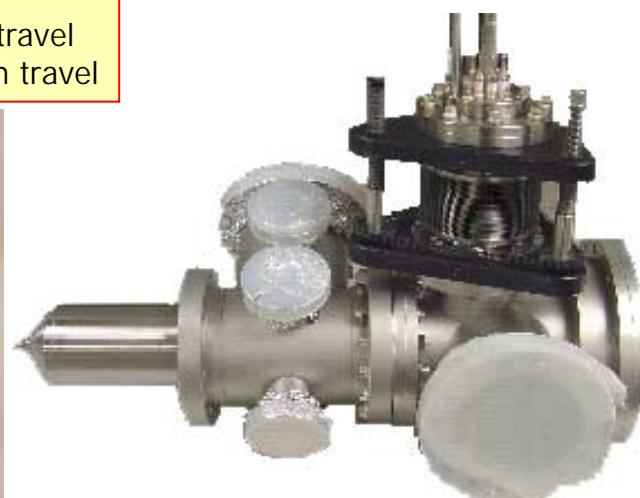


conventional X-ray source

our design: Electrostatic focusing



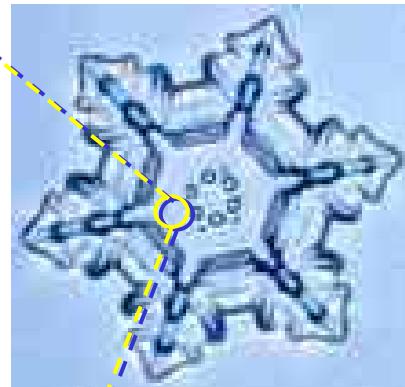
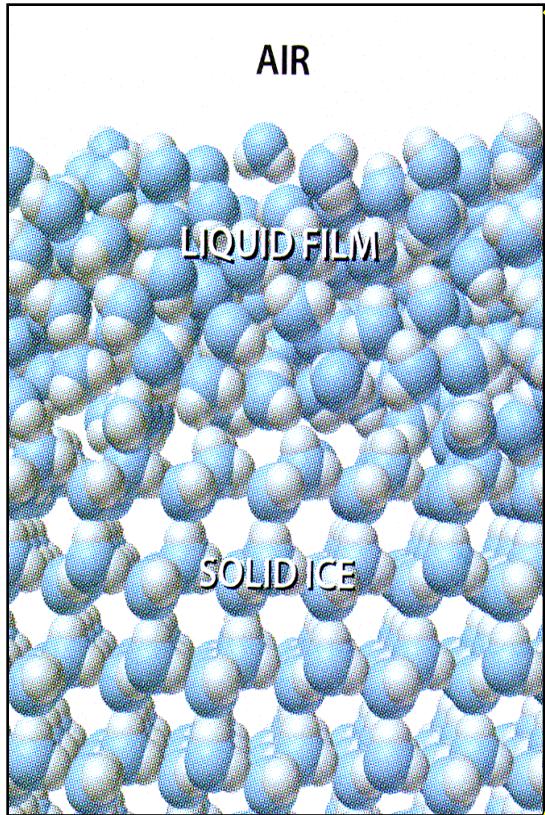
X-rays from synchrotron



Mark-II @ ALS 11.0.2

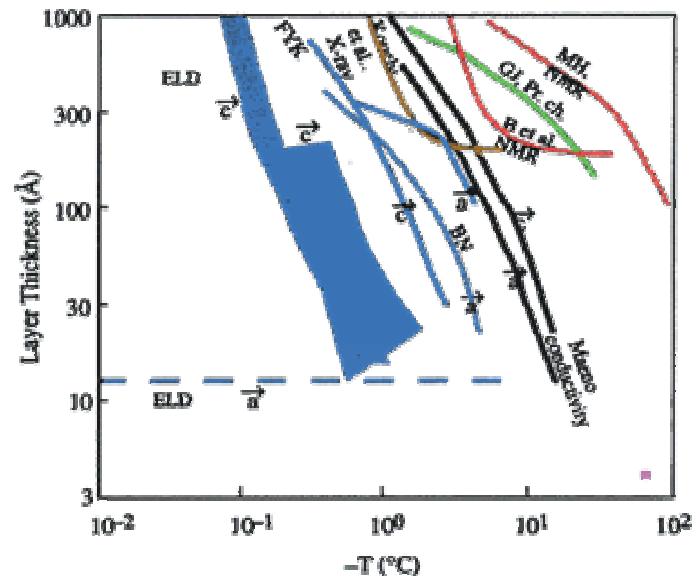
A differentially pumped electrostatic lens system for photoemission studies in the millibar range, D. Frank Ogletree, H. Bluhm, G. Lebedev, C. Fadley, Z. Hussain and M. Salmeron, Rev. Sci. Instr. 73, 3872 (2002)

The premelting phenomenon: Faraday *vs* Kelvin Does the melting of ice start at the surface ?

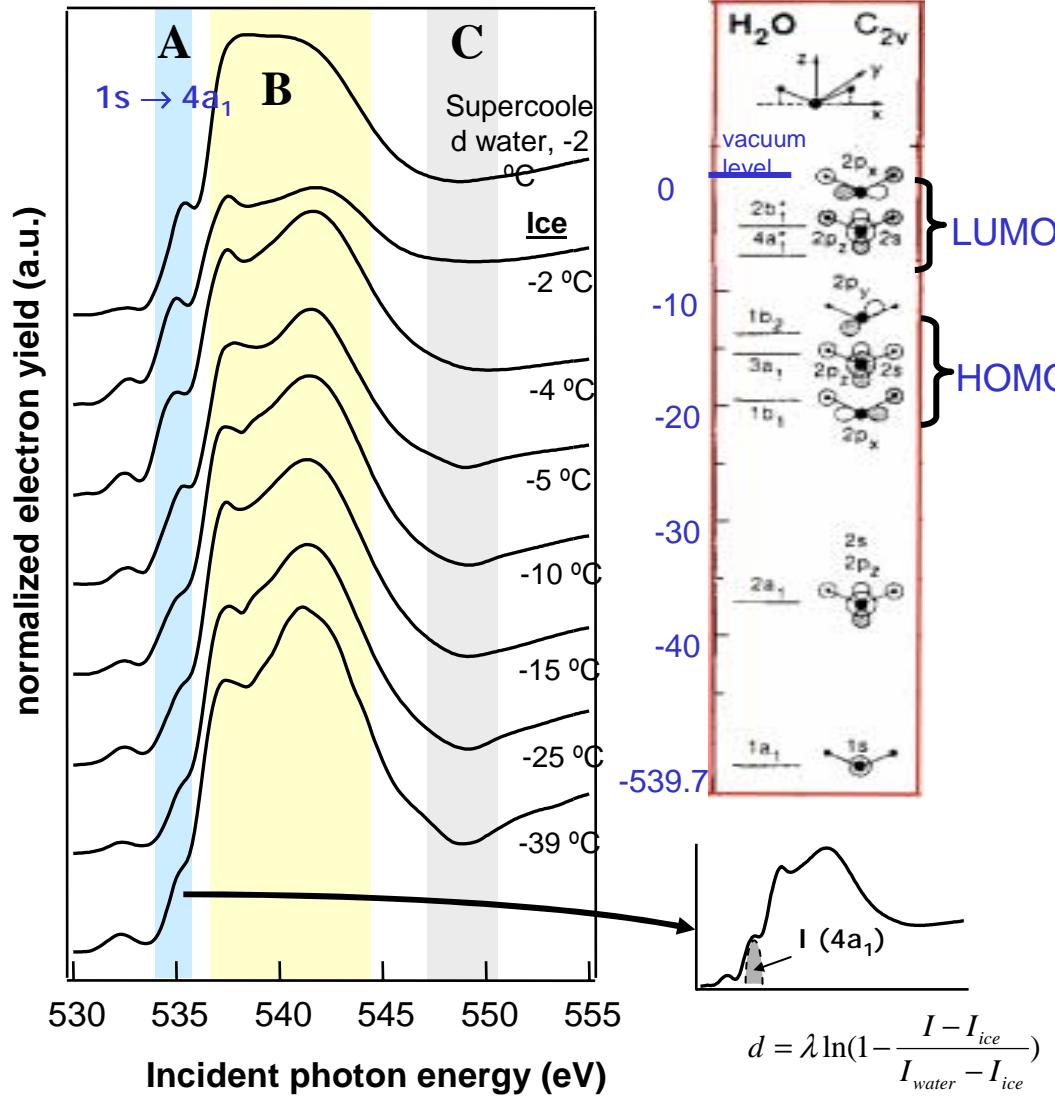


Found in the literature:

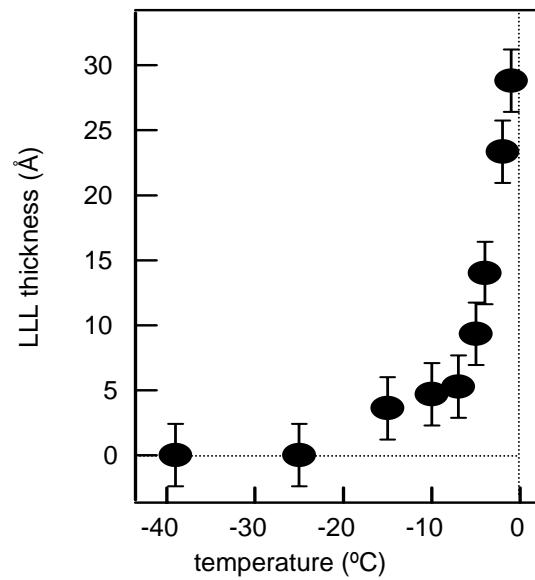
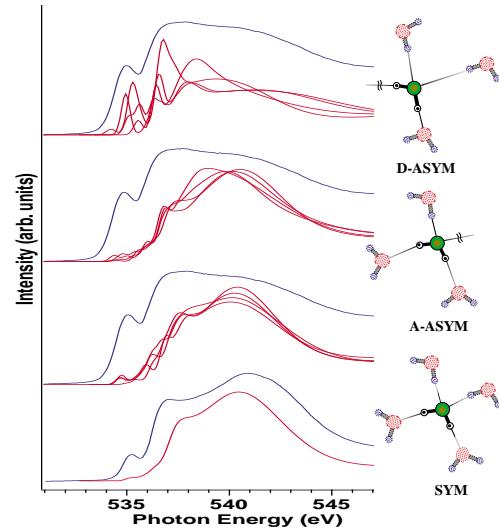
Thickness of the liquid-like layer



NEXAFS spectra of ice through the melting transition



Calculations by L.G.M. Pettersson, and A. Nilsson. J. Phys. Cond. Matt.



The premelting of ice studied with photoelectron spectroscopy
 H. Bluhm, D.F. Ogletree, C.S. Fadley, Z. Hussain and M. Salmeron.
J. Phys.: Condensed Matter **14**, L227 (2002)

Collaborators:

- | | |
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| • Eleonore Hebenstreit | |
| • Félix Requejo | Argentina |
| • Frank Ogletree | |
| • Sébastien Bardon | College de France |
| • Paulo Miranda | |
| • Prof. Ron Shen | |
| • Hendrick Bluhm | |
| • Mark Rose | |
| • Toshiyuki Mitsui | |
| • Evgeni Fomin | |
| • Frank Ogletree | |